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Bimetallic Effects on Ethylene Polymerization in the Presence of Amines: Inhibition of the Deactivation by Lewis Bases

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Abstract

Dinickel complexes supported by terphenyl ligands appended with phenoxy and imine donors were synthesized. Full substitution of the central arene blocks rotation around the aryl-aryl bond and allows for the isolation of atropisomers. The reported complexes perform ethylene polymerization in the presence of amines. The inhibiting effect of polar additives is up to 250 times lower on the *syn* isomer than the *anti* isomer. Comparisons with mononuclear systems indicate that the proximity of the metal centers leads to the observed inhibitory effect on the deactivation of the catalysts.

In recent years, a bioinspired strategy has been used for the design of multimetallic olefin polymerization catalysts in which the proximity of the active nuclei was intended to facilitate catalysis similar to the effects seen in many metalloproteins.[1,2] A wide variety of multimetallic olefin polymerization catalysts have been reported, with a broad range of distances between the metal centers and varying degrees of flexibility of the ancillary ligand.[3–9] Compared with monometallic counterparts, some bimetallic early transition metal catalysts have been reported to incorporate more comonomer and bulkier olefins in copolymerizations with ethylene.[9–14] Enhanced stability and activity have been reported as well.[1,2] Bimetallic catalysts based on late metals have been shown to increase the incorporation of olefins displaying polar moieties in copolymers with ethylene.[15] Although the nature of monomer interactions with bimetallic catalysts has been investigated in a few cases, studies of the effect of ligand rigidity and metal-metal distance on the polymerization outcome have been hindered by the scarcity of architectures in which these parameters can be controlled. Furthermore, the development of olefin polymerization catalysts that are not significantly affected by the presence of polar groups or that can incorporate polar monomers is of interest. Herein we report a series of bi- and monometallic nickel polymerization catalysts with rigid geometry and restricted intermetal distances. The dinickel catalyst with the metal centers found in proximity shows less inhibition of catalysis by amines, a favorable consequence of the bimetallic effect.

In designing a ligand for bimetallic catalysts, a 1,4-terphenyl moiety bearing four methyl substitutents on the central ring and one *ortho*-oxygen substitutent on each peripheral aryl ring was chosen as a suitably rigid backbone with restricted rotation around the aryl-aryl bonds. In the present work, salicylaldimine motifs were used as metal-binding sites on the outer aryl rings. For comparison, both bimetallic (**1-s** and **1-a**) and monometallic (**2-s** and **2-a**) species were prepared (Figure 1). Separation and purification of the atropisomers were achieved during the ligand synthesis. The nickel complexes were synthesized by reacting the

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Supporting Information Available: Experimental procedures, characterization data, and crystallographic details for **1-s**, **1-a**, and **1-a**-(1,1-dimethylpropylamine)$_2$ (CIF). This material is available free of charge via the internet at http://pubs.acs.org.

phenols with $NiMe_2$(tmeda) (tmeda=tetramethylethylenediamine) in the presence of pyridine. Structural assignment of each atropisomer was accomplished based on single crystal X-ray diffraction studies for the bimetallic systems (Figure 2) and ^1H–^1H NOESY NMR spectroscopy experiments for the monometallic systems.[16]

The solid-state structures of **1-s** and **1-a** reveal that the distance between the two metal centers in the *syn* isomer is 7.1 Å (average of the two molecules in the asymmetric unit) and in the *anti* isomer is 11.1 Å (Figure 2). The coordination environment around each metal is similar to previously reported nickel-phenoxyiminato complexes.[3–9,17] A slight distortion of the square planar geometry is notable in **1-s**; the pyridine ligands extend toward the second metal center and bend away due to steric repulsion. The structure of the *anti* isomer forbids cooperative reactivity because the two nickel centers are on opposite faces of the central arene. The monometallic analogs **2-s** and **2-a** emulate the steric effect of the terphenyl backbone without the presence of a second metal center. No interconversion of the *syn* and *anti* isomers of either the di- or mononickel complexes was observed over 13 hours at 50 °C.

Ethylene polymerization trials were performed with the isolated nickel complexes in toluene at 25 °C (Table 1). The present catalysts perform ethylene polymerization with activities similar to previously reported pyridine-ligated nickel-phenoxyiminato systems.[17,18] These experiments generate polyethylene with methyl branches (4 to 20 branches per 1000 carbon atoms).[19] Of the studied complexes, **1-s** is the slowest catalyst by five-fold, likely due to the increased steric bulk at the active site compared to the other systems. The neutral ligands coordinated to the nickel centers in **1-s** reach toward the second metal and hinder coordination of olefin. This proposal is supported by the distortion observed in the solid-state structure of **1-s**. Although the methoxy substitutent is located *syn* with respect to nickel, the steric bulk in **2-s** is likely not as large as that caused by the pyridine ligand bound to the second metal in the bimetallic system.

Ethylene polymerization trials in the presence of excess primary, secondary, and tertiary amines showed distinct inhibition trends (Table 1, 2). Complexes **1-a**, **2-a**, and **2-s** were inhibited by two orders of magnitude upon the addition of *N*,*N*-dimethylbutylamine, although the difference between **1-a** and **2-a** is not well understood in light of the similar steric environments (Table 2). This deactivation effect in the presence of added amines is similar to that reported previously for related mononickel systems.[20] In contrast, **1-s** was inhibited by only one order of magnitude. Consequently, in some cases (Table 1, entries 7, 8, 11–17), addition of a tertiary amine affords a *syn* catalyst that is more productive than the *anti* analog. The inhibition of the deactivation by amines observed only with **1-s** is hereafter referred to as the bimetallic effect. The ratio between the deactivation of **1-a** vs **1-s** isomers (R) provides a quantitative measure of this effect. Compared to **1-s**, catalyst **1-a** is inhibited 10–25 times more by triethylamine, *N*-methyldipropylamine, and *N*,*N*-dimethylbutylamine and up to 270 times more by tripropylamine. Differential inhibition by triethylamine was also observed at a shorter polymerization time that resulted in lower polymer yields for both **1-s** and **1-a**, indicating that the calculated R is not due decomposition of the catalysts at different rates (Table 1 entries 7, 8). The use of secondary or primary amines resulted in greater inhibition than the tertiary amines and, in all cases that yielded polymer, also displayed greater inhibition of **1-a** than of **1-s** (Table 1, entries 23, 25–28). Compared to **1-s**, catalyst **1-a** is inhibited approximately 10 times more with diisopropylamine and between 70 and 100 times more with 1,1-dimethylpropylamine and 1,1,3,3-tetramethylbutylamine (Table 1, entries 23, 25–28).

The effect of amines on **1-s** and **1-a** was studied by ^1H NMR spectroscopy. New Ni-CH_3 peaks were observed upon addition of one equivalent of 1,1-dimethylpropylamine, or of a large excess (≥100 equiv) of *N*,*N*-dimethylbutylamine or *N*,*N*-dimethylethylamine to **1-a**

and **1-s**, indicating competitive substitution of pyridine. *N*,*N*-dimethylbenzylamine does not displace pyridine even upon addition of 100 equivalents. All investigated amines displaced more pyridine from **1-a** than from **1-s**. Qualitatively, the binding ability was found to vary in the following order: pyridine ≈ 1,1-dimethylpropylamine ≫ *N*,*N*-dimethylbutylamine > *N*,*N*-dimethylethylamine ≫ *N*,*N*-dimethylbenzylamine (additional analysis included in SI). This trend mirrors the degree of inhibition recorded in ethylene polymerizations (Table 1, entries 4, 14, 19, 27, 29). The correlation suggests that stronger amine binding to nickel increases the bimetallic effect.

The observed catalytic behavior suggests a bimetallic effect on the extent of inhibition by added base. Polymer formation is dependent on coordination of olefin and turnover limiting olefin insertion into the metal-polymeryl bond.[21,22] Lewis bases compete with olefin for coordination to the metal and decrease the overall polymerization rate and polymer yield. [23–26] While steric bulk from the ligand framework could cause a decrease in deactivation by hindering the binding of amine, the studied complexes show similar inhibition profiles for **1-a**, **2-a**, and **2-s** in contrast to **1-s**. The proximal arrangement of the two metal centers in compound **1-s** is proposed to cause the difference in deactivation compared to **1-a**, **2-a**, or **2-s** (Figure 3). Simultaneously binding a bulky base to each nickel center of **1-s** is expected to be sterically disfavored compared to binding bases to all metal centers of **1-a**, **2-a**, or **2-s**. Hence, for **1-s**, ethylene may compete successfully with the amine for coordination to nickel. This has the net effect of inhibiting deactivation by the base for **1-s** compared to **1-a**, **2-a**, or **2-s**. Intriguingly, the proposed mechanism might also be relevant to the polymerization of olefins with binuclear cationic early transition metal catalysts, with the couteranions acting as inhibiting bases instead of amines.[11–14]

In agreement with the above mechanistic proposal, the extent of inhibition is dependent on the nature of the amine. The smallest amines induced a smaller difference between **1-s** and **1-a**. Binding of a smaller amine to one of the nickel centers of 2 **1-s** leaves space to bind a second amine to the other nickel center, thereby effecting inhibition similar to that seen for **1-a**. For several of the secondary and primary amines (dipropylamine, *N*-methylbutylamine, dibutylamine, and butylamine), tight coordination and insufficient bulk result in no polymerization (Table 1, entries 20–22,24). With intermediate-size tertiary amines, as the size increases, the inhibition of **1-s** is lowered compared to **1-a** ($NMeEt_2$ vs NEt_3 and $NMe_2{}^nBu$ vs $NMe_2{}^nPr$ vs $NMe{}^nPr_2$ vs $N{}^nPr_3$). This is consistent with the first coordinated amine hindering the binding of the second. Although X-ray quality crystals of the corresponding syn isomer have not been obtained, the solid-state structure of the 1,1-dimethylpropyl adduct of the bimetallic anti isomer highlights how the alkyl substituent of the primary amine extends toward the opposite aryl group, likely blocking the binding of a second amine in **1-s** (Figure 2). With larger amines ($NMe{}^nBu_2$ and $N{}^nBu_3$), it is proposed that binding of an amine at one nickel prevents the binding of ethylene at the second nickel of **1-s**; hence, the bimetallic effect is not apparent. Bulky and less basic *N*,*N*-dimethylbenzylamine and *N*,*N*-dimethylaniline show low inhibition likely because of weak binding to either isomer.

In summary, new mono- and dinickel ethylene polymerization catalysts are reported. The supporting ligands based on atropisomers of a locked terphenyl backbone allow for control of the relative position of the two catalytic centers. The *syn* bimetallic isomer shows less inhibition by added amines compared to the *anti* bimetallic and monometallic catalysts. The bimetallic effect observed with **1-s** is proposed to arise from the close proximity of the nickels disfavoring simultaneous ligation of base to both of the metal centers. This behavior is expected to have applications in the design of olefin polymerization catalysts with increased functional group tolerance and with potential for copolymerization of polar olefins by sterically favoring catalyst interaction with the olefin rather than polar moiety. Future

studies will explore these areas along with extending the terphenyl motif with restricted rotation to other multimetallic catalyst systems.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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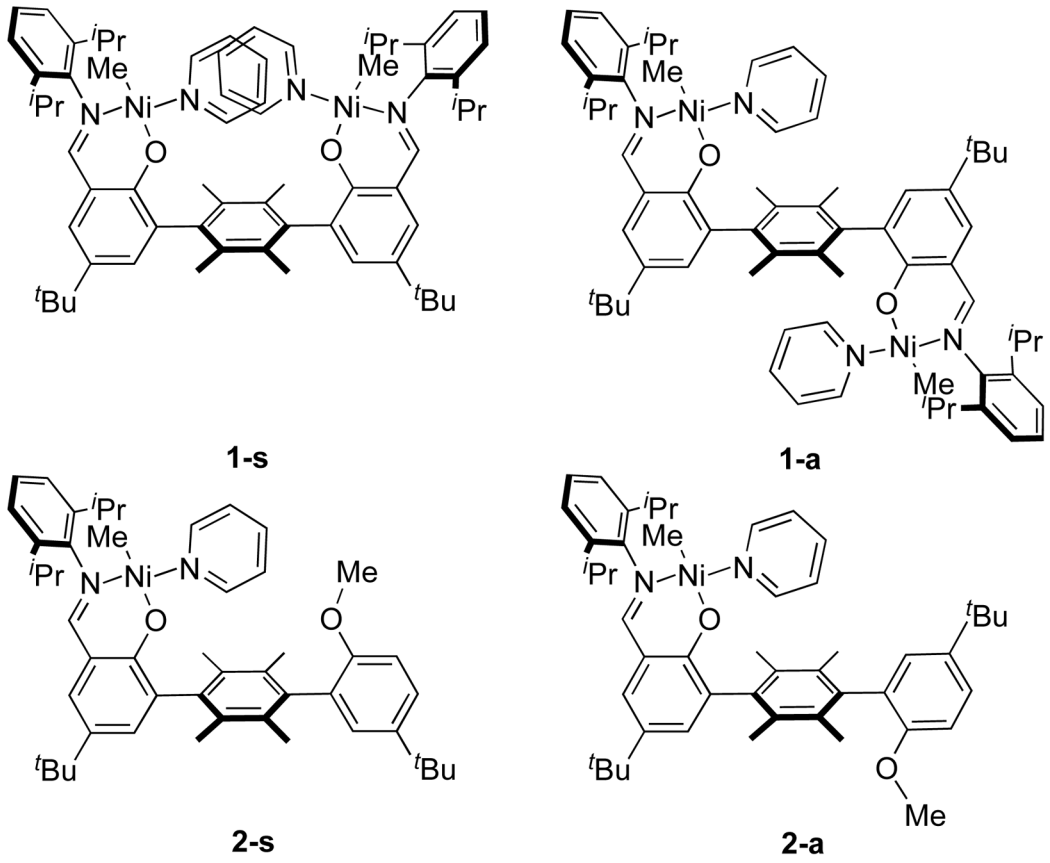

Figure 1.
Mono- and bimetallic catalysts for the polymerization of ethylene.

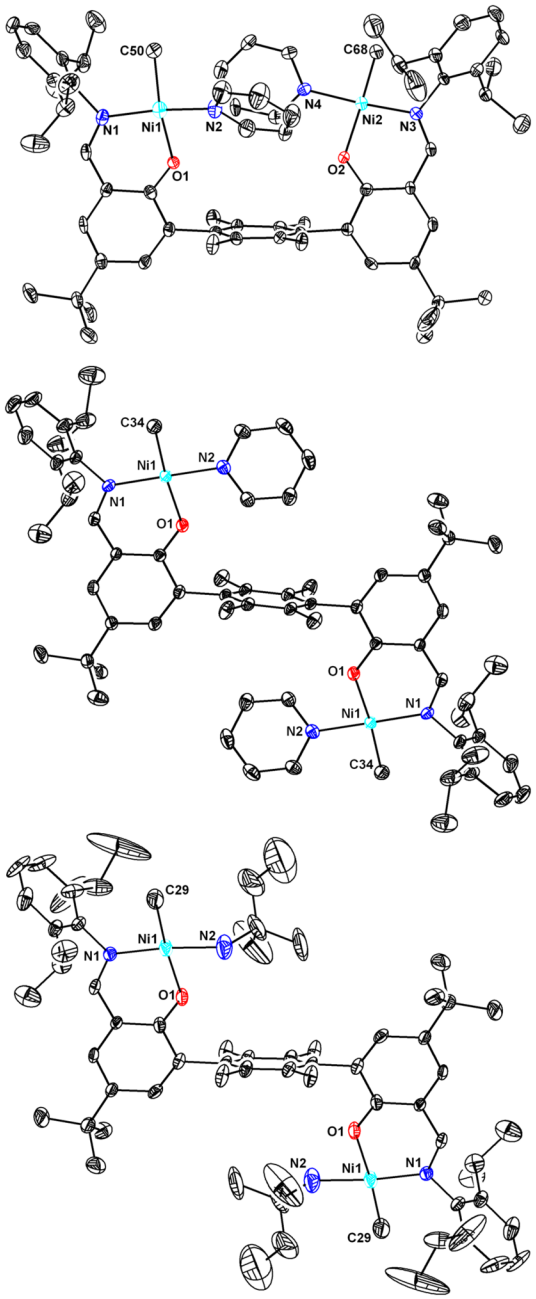

Figure 2.
Solid-state structures of **1-s** (top), **1-a** (center), and **1-a**-(1,1-dimethylpropylamine)$_2$ (bottom). Solvent molecules and hydrogen atoms were omitted for clarity.

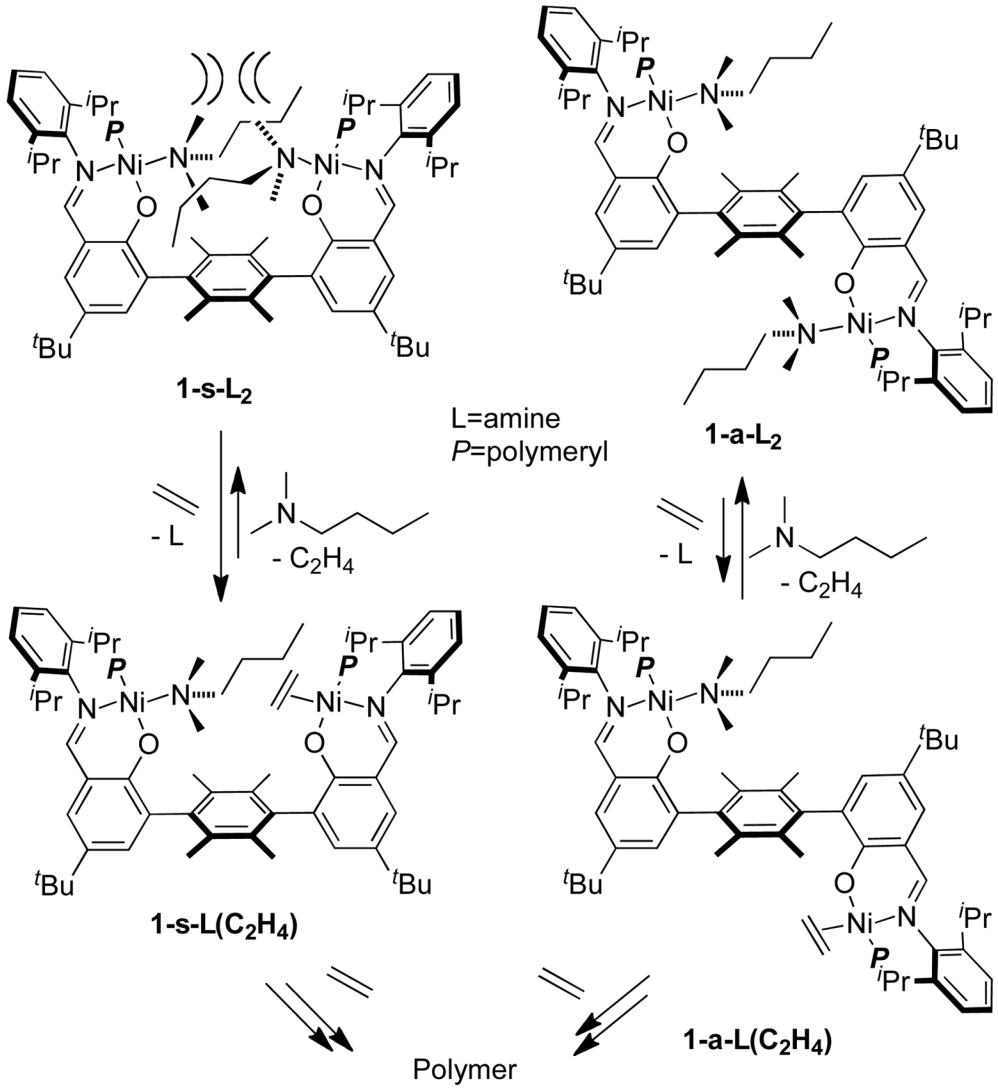

Figure 3.
Competition between ethylene and amine for binding to nickel in bimetallic complexes.

Table 1

Ethylene polymerization trials with 1-s and 1-a and polar additives.[a]

	Additive	Equiv	Yield (g)		TOF[b]		R[c]
			1-s	1-a	1-s	1-a	
1	none	n/a	0.574	3.415	341	2029	--
2	none	n/a	0.894	1.893[d]	531	2250[d]	--
3	NMe_2Et	500	0.150	1.440	89	856	0.5
4	NMe_2Et	500	0.148	1.032	88	613	0.7
5	NMe_2Et	5000	0.068	0.103	41	61	3.3
6	$NMeEt_2$	500	0.128	0.181	76	108	3.5
7	NEt_3	500	0.039	0.016	23	9	12.2
8	NEt_3	500	0.010[d]	0.006[d]	12[d]	7[d]	8.0
9	$NMe_2R^{1e,f}$	225	0.058	0.071	103	126	4.0
10	NMe_2R^{1e}	500	0.062	0.111	36	66	2.7
11	$NMe_2{}^nPr$	500	0.036	0.025	21	15	7.2
12	NMe^nPr_2	500	0.070	0.019	41	11	18.4
13	N^nPr_3	500	0.055	0.001	33	1	269
14	$NMe_2{}^nBu$	500	0.047	0.019	25	10	12.1
15	$NMe_2{}^nBu$	500	0.066	0.028	39	17	11.6
16	NMe^nBu_2	500	0.012	0.009	7	5	6.3
17	N^nBu_3	500	0.003	--[i]	2	--[i]	--
18	NMe_2Ph	500	0.619	2.867	367	1703	1.1
19	NMe_2Bz	500	0.252	1.330	150	790	0.9
20	HN^nPr_2	20	--[i]	--[i]	--[i]	--[i]	--
21	$HNMe^nBu$	20	--[i]	--[i]	--[i]	--[i]	--
22	HN^nBu_2	20	--[i]	--[i]	--[i]	--[i]	--

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	Additive	**Equiv**	**Yield (g)**		**TOF*b***		**R*c***
			1-s	**1-a**	**1-s**	**1-a**	
23	$HN^{i}Pr_2$	20	0.299	0.149	178	88	9.9
24	$H_2N^{n}Bu$	5	--*i*	--*i*	--*i*	--*i*	--
25	H_2NR^{2}*g*	50	0.011	--*i*	7	--*i*	--
26	H_2NR^{2}*g*	20	0.022	--*i*	13	--*i*	--
27	H_2NR^{2}*g*	5	0.080	0.003	48	2	136
28	H_2NR^{3}*h*	5	0.086	0.006	51	4	69.4
29	Pyridine	10	--*i*	--*i*	--*i*	--*i*	--

*a*All polymerizations were run for 3 hours at 25°C under 100 psig of ethylene in 25 ml of toluene with 10 μmol of dinickel complex. The number of equivalents of base listed is the number of equivalents per nickel.

*b*TOF = turnover frequency = $(\text{mol } C_2H_4)\times(\text{mol Ni})^{-1}\times h^{-1}$.

*c*R = ([TOF for **1-a** with no additive]/[TOF for **1-a** with additive])/ ([TOF for **1-s** with no additive]/[TOF for **1-s** with additive]).

*d*Polymerization was run for 1.5 hours.

*e*R1 = allyl.

*f*Polymerization was run for 1 hour.

*g*R2 = 1,1-dimethylpropyl.

*h*R3 = 1,1,3,3-tetramethylbutyl.

*i*Insufficient product to accurately mass (<1 mg).

Table 2

Ethylene polymerization trials with 500 equivalents of *N*,*N*-dimethylbutylamine per nickel.[a]

	Complex	Yield (g)	TOF[b]	R[d]
1	**1-s**	0.047	28	15
2	**1-s**	0.066	39	11
3	**1-a**	0.019	11	190
4	**1-a**	0.028	17	130
5	**2-s**	0.012	7	105
6	**2-s**	0.010	6	121
7	**2-a**	0.053	31	57
8	**2-a**	0.048	29	62

[a] All polymerizations were run for 3 hours at 25°C under 100 psig of ethylene in 25 ml of toluene with 20 μmol of nickel.

[b] TOF = turnover frequency = (mol C_2H_4)×(mol Ni)$^{-1}$×h^{-1}.

[d] R = (TOF with no additive)/(TOF with additive).